A STUDY OF DERMAL EXPOSURE OF FIELD WORKERS PICKING LEMONS TO RESIDUES OF CHLOROBENZILATE IN VENTURA COUNTY, CALIFORNIA

By

Keith T. Maddy, Staff Toxicologist
William Cusick, Field Supervisor
Susan Edmiston, Inspector
Catherine Cooper, Agricultural Chemist

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California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Unit
1220 N Street, Sacramento, California 95814

SUMMARY

The dermal exposure of field workers to chlorobenzilate residues was monitored while picking lemons in Ventura County, California in May 1980. Measurements were made by utilizing cloth pads placed over the thighs, chest, and sleeves of the workers' coveralls, gauze pads placed over the collar of the workers' coveralls, and hand-wash samples collected at the end of the work day. Chlorobenzilate had been applied to the orchard 18 days prior to the exposure period monitored. The calculated amount of chlorobenzilate that will reach the skin (calculated from residues found in cloth pads and hand washes) during a 7-hour work period for the 4 workers monitored ranged from 65.7 micrograms to 6.6 micrograms. The median exposure level per day was 36.5 micrograms. This level of exposure was considered to be so low that it would not be capable of causing any adverse health effects in these workers.

INTRODUCTION

Chlorobenzilate (ethyl 4,4'-dichlorobenzilate), an acaricide, was used in California primarily on cotton and citrus. It is registered under the trade name of Acaraben and is produced by Ciba-Giegy. In 1979, more than 128,216 pounds of chlorobenzilate was reportedly applied in California to approximately 60,000 acres.[1/] Since it was not restricted then, this figure may understate the actual use by as much as 50 percent.

Chlorobenzilate is not considered a hazardous material capable of causing acute illness if handled properly. Since 1975, no systemic illnesses caused by chlorobenzilate exposure have been reported by physicians in California. No illnesses with delayed onset and no deaths are known to have occurred from exposure to this chemical.

Laboratory test animals exposed to chlorobenzilate under certain conditions have been found to develop tumors in some body tissues as well as producing deformed testes. Other scientists believe that the evidence for carcinogenicity potential is quite weak. It is presumed by some investigators that these effects might occur in man with long-term exposure. In late 1979, the Environmental Protection Agency (EPA) cancelled all uses of chlorobenzilate except for the control of certain mites on citrus in Arizona, California, Florida, and Texas. California, early in 1980, imposed additional safe-use restrictions and made this chemical a restricted material. California requires that no one may enter a treated field during the 14 days following application if substantial foliage contact with the skin is expected to occur unless the same protective clothing is worn that is required for applicators. This protective clothing would include one-piece coveralls with long sleeves and long pants, a wide-brimmed hat, heavy-duty fabric work gloves, a respirator, and a face-shield or goggles.

MATERIALS AND METHODS

Dermal exposure of field workers picking lemons was measured 18 days after application by using cloth pads strategically[2/] attached to the worker's clothing and by collecting handwash samples at the completion of the day's work. The cloth pads were constructed in the following sequence, from inner to outer layer: (1) one sheet of paper, (2) one piece of aluminum foil, (3) a layer of 8-ply gauze, and (4) a layer of 6-ounce cotton duck cloth. The duck cloth and gauze were pre-rinsed with acetone or hexane to remove contaminants. The pads measured approximately 4 inches square and were held together with masking tape around the perimeter. The cloth pads were placed on each thigh, on both sides of the upper chest, and on each arm. Two rectangular pads, measuring approximately 6 x 2 inches, made without the duck cloth, were placed around the worker's neck. The pads that were placed on the chest and arms were made of a slightly lighter weight duck cloth similar to a typical worker's shirt.

At the completion of a day's work, the pads were carefully removed from the worker's clothing. The pads were then cut to remove the masking tape using a 7.0 square cm template for the 4 x 4 inch square pads, and a 12 cm x 5 cm template for the rectangular pads. The final surface areas for the square pads and the rectangular pads were 49 cm^2 and 60 cm^2, respectively.

1/ California Department of Food and Agriculture (1980).

2/ Durham and Wolfe (1962) and Wolfe (1967).

The layers of each sampling pad were separated and placed in glass jars as follows: (1) the cotton duck cloth and (2) the gauze and foil. The paper backing was discarded. The separate layers of each matched pair of thigh, chest, and arm pads were combined. (For example, the duck cloth layers from both the left and right thigh pads of an individual worker were combined.)

Handwash samples were collected to measure total hand exposure to chlorobenzilate. At the completion of the work day, a handwash sample was collected from each worker in the following manner: approximately 250 ml of deionized water, to which 1/8 tsp. of liquid Ivory soap had been added, was slowly poured over the worker's hands while held over a stainless steel bowl. The worker continuously rubbed his hands together to cover all surfaces with the soap solution. The wash water was then poured into a 16-ounce glass jar. The hands were then rinsed with 95% ethyl alcohol and handled in the same manner as the soap solution rinse water.

Inhalation exposure was assumed to be negligible based on previous worker reentry studies. The workers were in an orchard picking lemons for approximately 7-1/4 hours. They wore long-sleeved work shirts, work pants with long legs, and work boots. (Some wore hats.) The workers picked from 50 to 100 bags of lemons per day.

Chlorobenzilate had been applied 18 days before the study period. It had been applied at the rate of 1/4 pt of Acaraben 4E per 100 gallons. The mixture was applied at the rate of 1,800 gallons per acre. There were 2.25 pounds of actual chlorobenzilate applied per acre.

Chemical analytical procedures are contained in Appendix 1.

RESULTS

The results of the experimental data and information are summarized in the following tables:

Table 1 - Dermal exposure of workers determined by cloth and gauze sampling pads. Column A is the sampling period. Column B is the amount of chlorobenzilate found on the sampling pads recorded in micrograms per square centimeter. Column C is an estimate of the amount of chlorobenzilate exposure in micrograms per square centimeter adjusted for a typical full day's exposure (7 hours). Column D is an estimate of the average area of the skin of each body part in square centimeters.[2/] Column E is an estimate of the amount of chlorobenzilate to which the skin of each body part would be exposed, recorded in micrograms per day. Calculations for the neckfront and face use chlorobenzilate residues on the gauze pads on the neckfront to represent exposure of bare skin to airborne chlorobenzilate. (This assumes no face protection from respirator or shield.) Calculations for the neckback use chlorobenzilate residues on the gauze sample taken from the neckback. Calculations for the trunk, arms, and legs use the results from appropriate gauze pads to simulate skin covered with clothing. Column F is the sum of the exposure to the body parts, excluding the hands and inhalation exposure.

[2/] DuBois and DuBois (1916) and Berkow (1931)

Table 2 - Dermal exposure of the worker's hands using handwash sampling. Column A is the chlorobenzilate found in the rinse solutions after a handwash was completed, in micrograms per sample. Column B is total chlorobenzilate found in both handwash samples recorded in micrograms. Column C is the sampling period. Column D is an estimate (in micrograms per day) of the total daily exposure assuming a 7-hour work period.

It should be noted that this is an approximation. Further studies are needed to determine the best method for monitoring hand exposure.

Table 3 - Total dermal exposure to chlorobenzilate residues during a full day's work. Column A is the total exposure, excluding hand exposure, taken from Column F of Table 1. Column B is the total hand exposure taken from Column D of Table 2. Column C is the estimated total body exposure for a typical work day. (It is assumed that inhalation exposure is negligible.)

DISCUSSION

In laboratory studies, it was determined that test animals exposed to chlorobenzilate developed tumors and deformed testes. In 1979, the EPA cancelled all uses of chlorobenzilate, except those for control of certain mites on citrus in California, Florida, Texas, and Arizona. This chemical is now classified as a restricted material by the EPA and the CDFA.

In early 1980, the CDFA imposed additional safe use restrictions by emergency action. One of these restrictions was the setting of a reentry period of 14 days. If a worker enters the field before the 14-day reentry period is up and expects to have substantial contact with foliage, he is required to wear the same protective clothing as is required for applicators. This clothing includes one-piece coveralls with long sleeves and long pants, a wide-brimmed hat, heavy-duty fabric work gloves, a respirator, and a face shield or goggles.

Our study showed that the amount of chlorobenzilate that falls on the skin of a field worker picking lemons 18 days after application in a typical 7-hour work day ranged from 6.6 micrograms to 65.7 micrograms. Median exposure for the 4 workers was 36.5 micrograms. Inhalation exposure was assumed to be negligible, since chlorobenzilate has low volatility.

CONCLUSIONS

While picking lemons 18 days after application of chlorobenzilate, workers were exposed to levels of residues of this chemical that were so low they were considered to be without possible adverse health effects.

REFERENCES

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APPENDIX 1

Chlorobenzilate in Ethanol Handwashes

Ethanol handwash is analyzed directly by electron capture gas chromatography. In some cases the ethanol must first be filtered through glass wool. Results are reported as total number of micrograms present in sample.

Chlorobenzilate in Soap and Water Handwashes

Sampels of soap (Ivory) and water handwashes are extracted with nanograde hexane. Electron capture gas chromotography is used to analyze for the chlorobenzilate.

The volumn of sample is measured in a 500 ml graduated cylinder and then returned to the original sample jar. 10 mls of hexane is used to rinse the graduated cylinder, then added to sample along with 20 grams of anhydrous sodium sulfate. Jar is tightly capped with aluminum foil and screw cap lid and shaken vigorously for 1 minute. Sample is allowed to settle about 15 minutes, then, using a disposable pipet, hexane is drawn off. In some samples the emulsion may not break in the allotted time. In these cases draw off hexane plus emulsion to a test tube and add small amounts of sodium sulfate in increments, shaking vigorously each time. Extraction procedure is repeated with a 2nd portion of hexane. Analyze by electron capture gas chromatography and report results as micrograms per mls of handwash.

Chlorobenzilate on Cloth Patches

25 Mls of ethyl acetate is added to the sample jars containing the patches. The containers are sealed with aluminum foil and screw cap lid. Jars are rotated 1 hour. Gauze samples are treated in like manner. The extract is then analyzed directly by electron capture gas chromatography. Results are reported as micrograms per sample.

Chlorobenzilate: Gas Chromatographic Conditions

Instruments: Varian 3700 with ECD Detector at 250 degrees centigrade.

Perkin Elmer Sigma 2 with ECD Detector at 225 degrees centigrade.

Varian 2700 with ECD Detector at 200 degrees centigrade.

Columns : 6 foot 2mm glass columns

10% SP-2000 coated on chromsorb W-HP 210 degrees, 60 ml/min nitrogen carrier gas.
4% OV101 coated on 100/200 mesh gas chrome Q 220 degees, 30 ml/min nitrogen carrier gas.
3% SP-2250 coated on 100/120 supelcorport 200 degrees, 40 ml/min nitrogen carrier gas.

Under conditions listed above, chlorobenzilate comes out between 5-6.5 min.

Set up gas chromatograph to give 5-6.5 min retention time for chlorobenzilate peak. If samples have interfering peaks this time may need to be lengthened. Inject standards to condition column until same response is obtained for replicate injections.

Prepare standard curve to determine linearity and dilute or concentrate samples as necessary. Determine minimum detectible limit.

TABLE 1

Estimate of Dermal Exposure of Employees to Chlorobenzilate
While Picking Lemons 18 Days After Treatment in Ventura County, California

Worker Number	Skin Area Studied	Column A Hours of Exposure	Column B Amount of Chlorobenzilate on Cloth Pads (ug/cm^2) Inside Gauze	Column B Outside Cloth	Column C Amount of Chlorobenzilate on Cloth Pads Adjusted to 7-Hour Work Day (ug/cm^2) Inside Gauze	Column C Outside Cloth	Column D Area of Skin Surface (cm^2) Covered	Column D Bare	Column E Calculated Chlorobenzilate Dermal Exposure per 7-Hour Work Day (micrograms) Covered Skin	Column E Bare Skin	Column F Total Calculated Chlorobenzilate Dermal Exposure per 7-Hour Work Day (excluding hand exposure) (micrograms)
1	Arms	7.25	ND	0.0953	0	0.0920	1,210		0		
	Legs		0.0036	0.5334	0.0035	0.5150	2,322		8.07		
	Chest, Face Neckfront		ND	0.0726	0	0.0700	2,150	810	0	56.71	
	Back/ Neckback		NS	0.0033		0.0032	2,150	110		0.35	
	Total										65.13
2	Arms	7.25	ND	0.0678	0	0.0655	1,210		0		
	Legs		0.0051	0.0302	0.0048	0.0292	2,322		11.15		
	Chest, Face Neckfront		ND	0.0261	0	0.0252	2,150	810	0	20.41	
	Back/ Neckback		NS	0.0083		0.0080	2,150	110		0.88	
	Total										32.44
3	Arms	7.25	ND	0.0153	0	0.0148	1,210		0		
	Legs		0.0020	0.0147	0.0019	0.0142	2,322		4.41		
	Chest, Face Neckfront		ND	0.0412	0	0.0398	2,150	810	0	32.24	
	Back/ Neckback		NS	0.0040		0.0039	2,150	110		0.43	
	Total										37.08
4	Arms	7.25	ND	0.0103	0	0.0099	1,210		0		
	Legs		ND		0		2,322		0		
	Chest, Face Neckfront		ND	0.0073	0 0	0.0070	2,150	810	0	5.67	
	Back/ Neckback		NS	ND		0	2,150	110		0	
	Total										5.67

ND - None detected.
NS - No sample taken.

TABLE 2

Levels of Chlorobenzilate Found on the Hands of Employees After Picking Lemons

	COLUMN A		Column B	Column C	Column D
Worker No.	Handwash - Soap (ug/sample)	Handwash - Alcohol (ug/sample)	Total Chloro-benzilate Found On Hands (micrograms)	Hours of Exposure	Total Hand Expo-sure Adjusted to 7 Hours (micrograms)
1	0.56	ND	0.56	7.25	0.541
2	0.33	ND	0.33	7.25	0.319
3	1.4	1.77	3.17	7.25	3.061
4	0.92	ND	0.92	7.25	0.888

TABLE 3

Total Estimated Dermal Exposure of Lemon Pickers to Chlorobenzilate Residue

	Column A	Column B	Column C
Worker No.	Total Dermal Exposure for 7 Hours (exluding hand exposure) (micrograms)	Total Hand Exposure for 7 Hours (micrograms)	Total Calculated Chloro-benzilate Dermal Exposure Per 7-Hour Work Day (micrograms)
1	65.13	0.54	65.67
2	32.44	0.32	32.76
3	37.08	3.06	40.14
4	5.67	0.89	6.56